

Synthesis, Structural, Thermal and Biological Studies of Diaqua and Bis(triphenylphosphine) Substituted Late Transition Metal Complexes of 2-Aminopyridine

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Stable and neutral Co(II), Ni(II), Zn(II) and Cd(II) coordination complexes (**1-8**) of 2-aminopyridine were synthesized and characterized by various spectro-analytical techniques. The complexes **1-4** have octahedral geometry, with two 2-aminopyridine moieties in the same plane and two water molecules occupying the axial positions. Interesting structural variations were observed in the complexes when treated with calculated amount of triphenylphosphine (PPh₃) to replace the weaker water coordination. Atomic absorption and SEM techniques were also employed to analyze the metal content and surface nature of the complexes. ³¹P, ¹³C and ¹H NMR studies of PPh₃ coordinated complexes **5-8** confirmed the presence of phosphorous coordination through the axial positions. Finally, all the complexes showed potential activity in antimicrobial analysis against gram positive and negative bacteria.

Key Words: Co(II), Ni(II), Zn(II), Cd(II), 2-Aminopyridine, Antimicrobial agents, triphenylphosphine, Octahedral.

INTRODUCTION

In the last decade, there have been numerous attempts to produce ligand-exchanged late transition/inner transition metal complexes, which could not be produced by the direct preparation procedures¹⁻⁴. A ligand exchange reaction is the chemical change that occurs when one ligand is replaced by another relatively strong field ligand to produce novel metal complexes. Hydrated late transition metal ions, easily formed when a coordinatively unsaturated complex dissolves in water or in aqueous basic media, can be represented either as $L_4M^{n+}_{(aq)}$ or as $[ML_4(H_2O)_2]^{n+}_{(aq)}$ -because each metal ion is usually coordinated to two water molecules acting as ligands to suffice its maximum coordination valency. The exchange of ligands from an intact metal N-donor framework with labile ligands can be exploited as means to introduce functionalized/non-functionalized ligands into the complex architecture under mild conditions^{5,6}. The ligand exchange can occur even with inert transition metal complexes in a solvent dependent manner which is called as post synthetic exchange (PSE) and show that it provides access to the different transition metal complexes that are not readily prepared in high quality by solvothermal methods. Post synthetic exchange is an important post synthetic approach to the modification of transition metal complexes and the ligand exchange revealed by spectroscopic techniques requires a re-evaluation of the assumed stability of even the most robust

complexes. Recent activities in this area have enhanced the ligand exchange between metal-organic frameworks (MOFs) in both particle-to-particle and solution-to-particle fashions and show that ligand exchange can be eagerly achieved on an inert metal-organic framework⁷.

One of the most convenient approaches for the preparation of ligand exchanged late transition metal complexes has been the direct addition of strong coordinating species compared to the labile ligand(s) present in the coordination sphere. This exchange of ligands can easily be monitored by using various spectroscopic techniques. Triphenylphosphine, being the stronger coordinating species compared to water molecule are frequently being used for the ligand exchange/aryl-phosphorous insertion reactions. Until today, spectroscopic methods for monitoring the ligand exchange phenomena have been regarded as the most effective methods. Precedent for the findings of Morel and co-workers⁸ was provided by several earlier studies that demonstrated the lability of fluorescent ligand in a series of copper complexes. The triphenylphosphine exchange process described here is perhaps a more exciting finding, due to the larger stability and inertness of the derived complexes. We demonstrate that aqua substituted late transition metal complexes of 2-aminopyridine provides a powerful post synthetic method for the preparation of bis-triphenylphosphine substituted complexes.

EXPERIMENTAL

All the chemicals and solvents were obtained from commercial sources and used as received without further purifications. Metal chlorides *viz.*, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and ZnCl_2 were purchased from system chem AR and R and M chemicals. Metal contents were estimated using a Perkin-Elmer Analyst 200-atomic absorption spectrometer. Melting points of the compounds were determined by using a Gallenkamp apparatus. FTIR spectra were recorded in a KBr disc matrix using a Perkin-Elmer-2000 Spectrometer in the 4000-400 cm^{-1} range. UV-Visible spectra were recorded on a Hitachi U-2000 Spectrophotometer in the range of 1,000-200 nm. The ^{31}P , ^{13}C and ^1H NMR spectra were recorded in $\text{DMSO}-d_6$ on a Bruker-500 MHz Ascend and Avance 300 MHz spectrometers at ambient temperature using TMS as internal reference. ^1H and ^{13}C NMR peaks are labeled as singlet (s), doublet (d), triplet (t) and multiplet (m), chemical shifts are referenced with respect to solvent signals. All the compounds were analyzed for carbon, hydrogen and nitrogen by Perkin-Elmer series II, 2400 microanalyzer. TG and DTA measurements were recorded in nitrogen atmosphere on a TGA/SDTA 851E Mettler Telado analyzer. Surface studies were performed using a Leo supra-50 vp carl-zeiss SMT scanning electron microscope.

Syntheses

Preparation of bis-(2-aminopyridine)-diaqua complexes

General procedure: The complexes were prepared by the drop-wise addition of a methanolic solution of the metal(II) chloride (0.01 mol, 1 equivalent) with constant stirring to a basic aqueous solution of 2-aminopyridine (0.02 mol, 1.88 g) with KOH (0.02 mol, 1.12 g). The reaction mixture was heated at 50 °C for 20 min than allowed to cool to room temperature. The resulting precipitate collected, washed with limited amount of ethanol, water and dried at room temperature (**Scheme-I**).

[Bis-(2-aminopyridine)Co(II)diaqua] (1): Yield: 95.1 %, m.p. *ca.* 98 °C (decomposition temperature). Elemental analysis: found (calcd.) (%): C 42.3 (42.7), H 5.5 (5.0) and N 20.4 (19.9). FTIR (KBr disc, ν_{max} , cm^{-1}): *ca.* 3410 (N-H, amine), 1542 (C=N, pyridine ring), 1413 (C=C, pyridine ring) and 540 (Co-N).

[Bis-(2-aminopyridine)Ni(II)diaqua] (2): Yield: 89.4 %, m.p. *ca.* 97 °C (decomposition temperature). Elemental analysis: found (calcd.) (%): C 43.0 (42.7), H 5.5 (5.0) and N 19.7 (19.8). FTIR (KBr disc, ν_{max} , cm^{-1}): 3435 (N-H, amine), *ca.* 1550 (C=N, pyridine ring), 1358 (C=C, pyridine ring) and 522 (Ni-N).

[Bis-(2-aminopyridine)Zn(II)diaqua] (3): Yield: 92.6 %, m.p. *ca.* 98 °C (decomposition temperature). Elemental analysis: found (calcd.) (%): C 41.4 (41.8), H 5.3 (4.9) and N 19.9 (19.5). FTIR (KBr disc, ν_{max} , cm^{-1}): *ca.* 3400 (N-H, amine), *ca.* 1570 (C=N, pyridine ring), 1545 (C=C, pyridine ring) and 520 (Zn-N). ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 2.9 (s, 1H, amine-NH), 7.4 (t, 2H, aromatic H) and 7.7 (d, 4H, aromatic H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 128.5, 128.9, 129.4, 132.1, 132.5 and 132.7 (aromatic C).

[Bis-(2-aminopyridine)Cd(II)diaqua] (4): Yield: 94.2 %, m.p. *ca.* 94 °C (decomposition temperature). Elemental analysis: found (calcd.) (%): C 36.4 (35.9), H 4.7 (4.2) and N 16.5 (16.7). FTIR (KBr disc, ν_{max} , cm^{-1}): *ca.* 3450 (N-H, amine), *ca.* 1580 (C=N, pyridine ring), 1435 (C=C, pyridine ring) and 540 (Cd-N). ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 2.4 (s, 1H, amine-NH), 7.6 (t, 2H, aromatic H) and 7.84 (d, 4H, aromatic H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 127.8, 128.6, 129.4, 132.6, 132.7 and 132.9 (aromatic C).

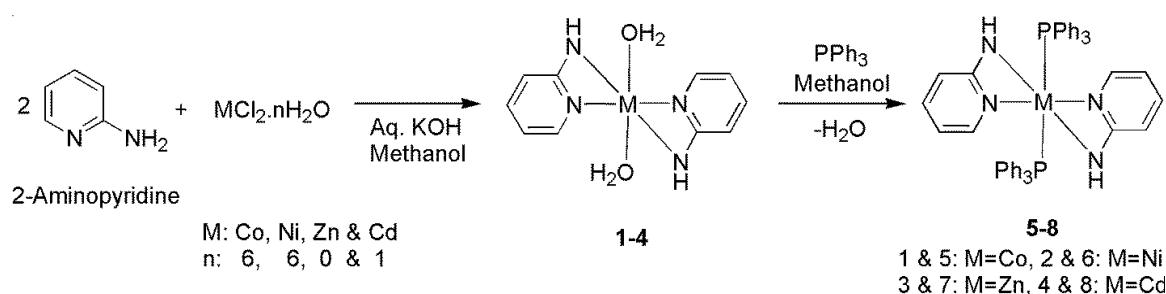
Preparation of bis-(2-aminopyridine)-bis-(triphenyl phosphine) complexes

General procedure: An ethanolic solution of bis-(2-aminopyridine)diaqua complex (1 mmol, 1 equivalent) was added to an acetone solution of triphenylphosphine (2 mmol, 0.53 g) with constant stirring over 0.5 h than stirring was continued for another 2 h at room temperature. The resulting precipitates were filtered off, washed several times with water, acetone then were dried in an oven at 120 °C.

[Bis-(2-aminopyridine)-bis-(triphenylphosphine)-Co(II)] (5): Yield: 82.0 %, m.p. > 300 °C. Elemental analysis: found (calcd.) (%): C 20.3 (20.8), H 14.8 (14.0) and N 20.6 (20.3). FTIR (KBr disc, ν_{max} , cm^{-1}): 3455 (N-H, amine), 1547 (C=N, pyridine ring), 1433 (C=C, pyridine ring), 544 (Co-N) and 488 (Co-P).

[Bis-(2-aminopyridine)-bis-(triphenylphosphine)-Ni(II)] (6): Yield: 74.4 %, m.p. > 300 °C. Elemental analysis: found (calcd.) (%): C 20.3 (20.5), H 14.8 (15.3) and N 20.6 (20.3). FTIR (KBr disc, ν_{max} , cm^{-1}): 3446 (N-H, amine), 1547 (C=N, pyridine ring), 1348 (C=C, pyridine ring), 522 (Ni-N) and 483 (Ni-P).

[Bis-(2-aminopyridine)-bis-(triphenylphosphine)-Zn(II)] (7): Yield: 79.1 %, m.p. > 300 °C. Elemental analysis: Found (calcd.) (%): C 19.1 (18.5), H 15.1 (14.6) and N 21.2 (21.0). FTIR (KBr disc, ν_{max} , cm^{-1}): 3498 (N-H, amine), 1585 (C=N, pyridine ring), 1547 (C=C, pyridine ring), 523 (Zn-N) and 496 (Zn-P). ^1H NMR ($\text{DMSO}-d_6$) δ ppm: 2.91 (s, 1H, amine-NH), 7.3 (t, 2H, aromatic H) and 7.6 (d, 4H, aromatic H). ^{13}C NMR ($\text{DMSO}-d_6$) δ ppm: 129.5, 129.7, 129.9, 132.3,



Scheme-I: Synthesis of diaqua and bis(triphenylphosphine) substituted complexes 1-8

132.5 and 132.9 (aromatic C). ^{31}P NMR (DMSO- d_6) δ ppm: -5.75 (s, axial P) and 27.14 (s, axial P).

[Bis-(2-aminopyridine)-bis-(triphenylphosphine)-Cd(II)] (8): Yield: 64.0 %, m.p. >300 °C. Elemental analysis: found (calcd.) (%): C 16.2 (16.9), H 12.7 (12.4) and N 18.3 (17.8). FTIR (KBr disc, ν_{max} , cm^{-1}): 3449 (N-H, amine), 1583 (C=N, pyridine ring), 1433 (C=C, pyridine ring), 540 (Cd-N) and 495 (Cd-P). ^1H NMR (DMSO- d_6) δ ppm: 2.3 (s, 1H, amine-NH), 7.55 (t, 2H, aromatic H) and 7.64 (d, 4H, aromatic H). ^{13}C NMR (DMSO- d_6) δ ppm: 129.5, 129.7, 129.8, 132.2, 132.4 and 132.9 (aromatic C). ^{31}P NMR (DMSO- d_6) δ ppm: -5.63 (s, axial P) and 27.02 (s, axial P).

Antibiogram tests: The stock solution of all compounds was prepared using dimethyl sulphoxide. For disc diffusion method, a loopful of the bacterial strain was inoculated into the nutrient rich medium and was incubated for 16 h at 37 °C. About 50 μL of the suspension was applied uniformly on the surface of the nutrient agar plate before placing the sterilized antimicrobial assay discs on the plate (4 per plate) and different volumes of samples (3, 6, 9 and 12 μL) were loaded on the surface of the discs. The plates were incubated at 37 °C for 24 h. Later, the average zone of inhibition was measured with a ruler with up to 1 mm of resolution. For viable cell count method, the concentrations of the tested compound were 100, 200, 400 and 800 $\mu\text{g mL}^{-1}$. The bacterial strain was inoculated into the nutrient rich medium and was incubated for 16 h at 37 °C. After the serial dilution (10^6 CFU/mL) was done, about 60 μL of bacterial suspension was transferred into the universal bottles containing 3 mL of nutrient broth followed by the sample suspension. The incubation was carried out for 5 h at 37 °C and 50 μL of culture was uniformly spread on the nutrient agar which was incubated at 37 °C for 24 h. The incubation of the culture in the universal bottles was continued for 24 h. MIC (minimum inhibitory concentration) was determined based on the lowest concentration of the samples that inhibits the growth of the bacterial strain. For growth inhibitory concentrations, the presence of viable microorganisms was tested and the lowest concentration causing bactericidal effect was reported as MBC (minimum bactericidal concentration).

RESULTS AND DISCUSSION

All of these novel complexes are insoluble in most common organic solvents such as benzene, acetonitrile, ethanol and chloroform, but completely soluble in DMSO and DMF. Numerous attempts to grow single crystals suitable for the X-ray diffraction analysis ended with the negative results as these complexes are highly amorphous in nature.

Abstraction of a proton from a primary amine derivative using a strong base like KOH certainly increases its basic nature and reactivity towards acidic metal ions. The diaqua complexes **1-4** were prepared by the reaction of 2-aminopyridine and acidic metal salts in a basic medium. KOH was used as a strong base to abstract the amine proton of 2-aminopyridine followed by the addition of methanolic solution of metal salts in 2:1 ratio. In order to acquire the octahedral geometry, the axial coordination of two water molecules was found in all the complexes. Later, the diaqua complexes were treated with more reactive triphenylphosphine for the ligand exchange reactions

in alcoholic medium. However, the kinetics of the ligand exchange reactions cannot be studied as the reaction proceeds in a very vigorous manner.

FTIR spectra of the complexes **1-8** show that 2-aminopyridine behaves as a monobasic bidentate chelate and coordinating through the pyridine and amino nitrogen atoms. The latter is *via* deprotonation along with the formation of hydrogen chloride which was easily neutralized by KOH. The spectrum of 2-aminopyridine displays two distinct IR bands at 3326 and 1619 cm^{-1} corresponding to the stretching vibrations of amine functionality and pyridine ring, respectively. These vibrations suffered positive as well as negative shifts in the complex spectra indicating their involvement in the coordination. The pyridine ring vibrations appeared in the range 1547-1585 cm^{-1} ^{9,10} and the decreased intensity of -NH bands in the spectra of **1-8** indicating the deprotonation of amine group upon coordination with the metal centers. Bands at around 540 and 490 cm^{-1} were attributed to metal-nitrogen and metal-phosphorous fragments, respectively. Apart from these, spectra also evidenced the presence of bands at around 1480 and 2900 cm^{-1} , which were collectively attributed to the stretching vibrations of C=C and C-H bonds, respectively (Figs. 1 and 2).

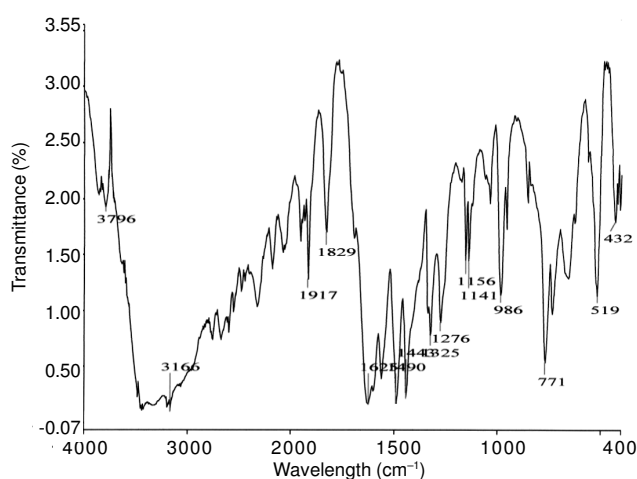


Fig. 1. FTIR spectrum of 2-aminopyridine

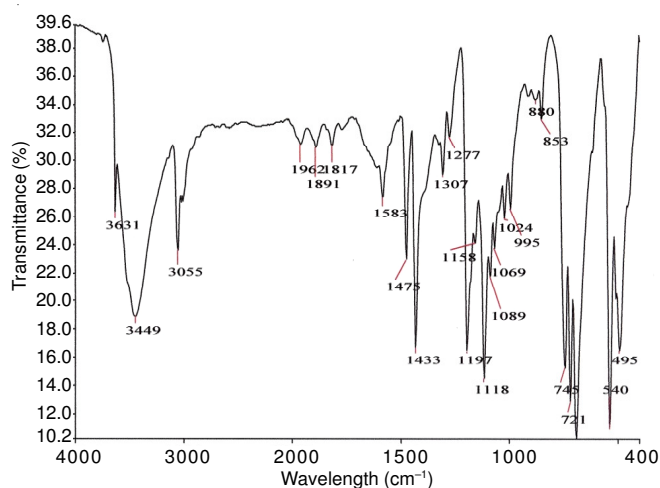


Fig. 2. FTIR spectrum of the complex **8**

^1H , ^{13}C and ^{31}P NMR spectra of Zn(II) and Cd(II) complexes were recorded in DMSO- d_6 solvent over the range of δ 0-16, 0-200 and -10-100, respectively. ^1H NMR spectra of the complexes showed a sharp singlet peak in the upfield region (δ 2.3-2.9) and was assigned to the resonance of amine protons. This shift mainly depends on the extent of nitrogen lone pair overlap on metal ions¹¹. The spectra also evidenced a set of triplet and doublet aromatic peaks in the range 7.3-7.7 δ ppm. The ^{13}C NMR signals due to aromatic carbon atoms found in the range 129-133 δ ppm which are consistent with the pyridine derived systems. The ^{31}P NMR spectra of the complexes **7** and **8** exhibit intensive resonance signals at δ -5.6 and 27.1 due to axial phosphorous coordination. Axial coordination of the phosphorous species is further confirmed by the appearance of two distinct peaks which is consistent with the reported examples.

The electronic absorption spectra of all the compounds were recorded in DMSO over the range 1000-200 nm. Complexes **1-8** show two distinct maxima at around 210 and 298 nm assigned to charge transfer transitions from the pyridine and amine nitrogen atoms. These bands are slightly red-shifted compared to π - π^* and n - π^* transition bands of 2-aminopyridine, indicating coordination of the pyridine and amine nitrogen atoms to the metal centers¹². Cobalt and nickel complexes show intense bands at around 505, 540 and 500, 565, 610 nm, respectively, assigned to the d - d transitions of Co(II) and Ni(II) ions^{13,14}. These absorption values are well within the range for reported octahedral Co(II) and Ni(II) complexes. In case of all diamagnetic complexes, the band appeared at around 290 nm ascribed to the charge transfer transitions and no band is found at the lesser energy region as expected.

The thermal behaviour of the complexes was studied in the temperature range 30-1000 °C at nitrogen atmosphere and the data is tabulated in Table-1. The thermal behaviours of all aqua coordinated complexes **1-4** are almost similar and show weight loss in three significant steps. The first weight loss corresponding to the elimination of two water molecules observed in the temperature range 95-110 °C and attributed as the first decomposition by the loss of two coordinated water molecules. The corresponding DTA curves show an endothermic peak at 120 °C which confirms the loss of coordinated water molecules¹⁵. In the second and third steps, the weight losses were observed in the temperature ranges 150-250 and 250-375 °C and attributed to the combined weight loss of ligand part. However, in case of triphenylphosphine coordinated complexes **5-8**, the weight loss was observed in two different steps. The first weight loss corresponds to the removal of two triphenylphosphine molecules in the temperature range 65-250 °C which is further supported by the exothermic DTA signals. The subsequent step is attributed to the loss of ligand part in the temperature range 250-890 °C. Finally, the thermograms become plateau due to the formation of stable metal oxides.

Particle size determination study of one of the cadmium complex using SEM was carried out to check the self assembly properties. However, the observed picture suggests the aggregation of the complex molecules at the surface with a much bigger molecular size of about 10 μm . The SEM picture of the complex **8** is shown in Fig. 3.

Complex	Decomposition Stage	Temp. range (°C)	Thermal effect	Weight losses (%)	Residue (%)
5	1	60-250	Exo	23.2	7.15
	2	250-890	Exo	42.5	Co ₂ O ₃
6	1	65-250	Exo	24.7	9.24
	2	250-298	Exo	44.1	NiO
7	1	50-190	Exo	27.6	10.2
	2	190-895	Exo	43.7	ZnO
8	1	70-210	Endo	28.1	13.45
	2	210-896	Exo	47.7	CdO

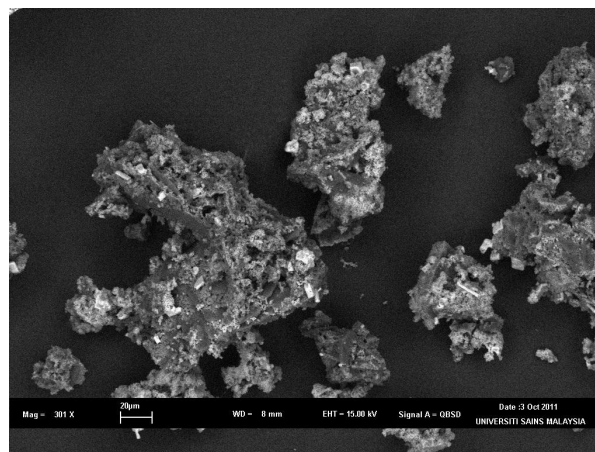


Fig. 3. SEM picture of the complex **8**

Antibiogram studies: All the compounds tested against a gram negative bacterium *viz.*, *Escherichia coli* and a gram positive bacterium *viz.*, *Staphylococcus aureus* were found to be active at all the tested concentrations. Antibacterial activity of the compounds was tested by the disc diffusion, cell count and colony formation methods. The results have been tabulated in Tables 2-5. The phosphorous coordinated complexes **5-8** show good activity with compared to aqua complexes **1-4**. The increased activity may be originated from the phosphorous insertion at the axial position of the regular octahedron.

According to the results of disc diffusion methods, the antimicrobial activity of cadmium complex **8** and the zinc complex **7** are the highest and showed good inhibition of 35 ± 1 and 42 ± 2 mm against the bacteria *E. coli* and *S. aureus*, respectively. Based on the observation, the diameter of zone of inhibition was increased as the volume of the antimicrobial agents was increased from 3-12 μL . All the other compounds showed good inhibition against both the bacteria since the diameter of the zone is in a narrow range. The entire antimicrobial agents have the same value of MIC and MBC against

Complex	<i>E. coli</i> ($\mu\text{g mL}^{-1}$)		<i>S. aureus</i> ($\mu\text{g mL}^{-1}$)	
	MIC	MBC	MIC	MBC
5	100	200	100	200
6	100	200	100	200
7	100	200	100	200
8	100	200	100	200

TABLE-3
ANTIMICROBIAL ACTIVITY AGAINST *E. coli*
AND *S. aureus* BY DISC DIFFUSION METHOD

Complex	Bacterium	Diameter (mm)			
		3 μ L	6 μ L	9 μ L	12 μ L
5	<i>E. coli</i>	12 \pm 1	23 \pm 2	29 \pm 1	31 \pm 1
6		24 \pm 1	27 \pm 2	30 \pm 2	32 \pm 2
7		24 \pm 1	27 \pm 1	28 \pm 2	31 \pm 2
8		22 \pm 2	30 \pm 1	33 \pm 1	35 \pm 1
5	<i>S. aureus</i>	34 \pm 1	36 \pm 1	38 \pm 2	41 \pm 2
6		30 \pm 2	33 \pm 1	35 \pm 2	37 \pm 1
7		38 \pm 1	40 \pm 2	41 \pm 1	42 \pm 2
8		24 \pm 1	30 \pm 1	34 \pm 1	38 \pm 2

TABLE-4
COLONY FORMING UNIT PER mL (CFU/mL) OF
DIFFERENT CONCENTRATIONS OF ANTIMICROBIAL
AGENTS AGAINST *E. coli* AND *S. aureus*

Complex	Bacterium	CFU (mL) (10^4)			
		Concentration (μ g mL $^{-1}$)			
		100	200	400	800
5	<i>E. coli</i>	20 \pm 1	0	0	0
6		14 \pm 1	0	0	0
7		18 \pm 1	0	0	0
8		6 \pm 1	0	0	0
5	<i>S. aureus</i>	8 \pm 1	0	0	0
6		12 \pm 1	0	0	0
7		4 \pm 1	0	0	0
8		11 \pm 1	0	0	0

TABLE-5
CELL COUNT OF *E. coli* AND *S. aureus* AFTER TREATED AT
DIFFERENT CONCENTRATIONS OF COMPLEXES

Complex	Bacterium	Concentration (μ g mL $^{-1}$)			
		100	200	400	800
5	<i>E. coli</i>	5.3	0	0	0
6		5.1	0	0	0
7		4.8	0	0	0
8		5.3	0	0	0
5	<i>S. aureus</i>	4.9	0	0	0
6		5.1	0	0	0
7		4.6	0	0	0
8		5.0	0	0	0

both, the gram negative and gram positive bacteria. Therefore, it was obvious that these antimicrobial agents were good inhibitors for both of the bacteria. The colony forming unit per mL (CFU/mL) was decreased as the concentration of the compounds was increased. No viable colony of *E. coli* or *S. aureus* was observed for the compounds at the concentrations more than 100 μ g mL $^{-1}$.

Conclusion

A series of diaqua (**1-4**) and *bis*-(triphenylphosphine) (**5-8**) complexes of late transition metals have been prepared and successfully characterized using different spectro-analytical techniques. The complexes **1-4** have been subjected to ligand exchange reaction using methanolic solution of triphenylphosphine under mild conditions to yield *bis*-(triphenylphosphine) substituted complexes **5-8**. All complexes were screened for the antibiogram activity using a gram negative *viz.*, *E. coli* and a gram positive bacterium *viz.*, *S. aureus* by different methods. In all the types of screening tests, phosphorous substituted zinc and cadmium complexes show good activity against both the bacteria.

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